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(54) Calculating alloy composition

(57) A method of making a γ' precipitation strengthening type Ni base superalloy and apparatus for determining the proportion of constituent elements of the alloy are disclosed. The apparatus includes a memory which stores proportions of constituent elements of the alloy, and an input unit for entering the composition of an alloy and storing it into the memory or for entering required performance data. A calculating unit employs a structural factor equation and a property equation and calculates structural factors from the stored proportions and calculates properties of the alloy based on the stored proportions and the calculated structural factors and displays them and/or outputs them for production process control. By an iterative search process alloys can be made having desired properties.

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DETERMINING COMPOSITION OF A γ' PRECIPITATION
STRENGTHENING Ni BASE SUPERALLOY

This invention relates to a method of making a γ' precipitation strengthening Ni base superalloy and to a device for determining the proportion of constituent elements for use in the production of a γ' precipitation strengthening Ni base superalloy which in its preferred form can conveniently and effectively analyze various properties of alloys, including thermal fatigue resistance, high-temperature tensile property, and high temperature corrosion resistance, and determine the composition of a new γ' precipitation strengthening Ni base superalloy which meets the required performance.

Conventionally, a γ' precipitation strengthening Ni base superalloy has been known as a heat resisting alloy having a superior high-temperature strength, and has been in widespread use in the high-temperature members of jet engines, power generating gas turbines and other heat engines. It is especially receiving attention as a material indispensable to the buckets of heat engines. It is of critical importance for the bucket material for the heat engine to offer excellent high-temperature strength. This property of the bucket material has significant effects upon the output, efficiency and other performances of heat engines. On the other hand, various properties, such as oxidation resistance, sulfidation corrosion resistance, and creep resistance, are required of bucket materials. As the development of aerospace technology is growing up, it has highly been desirable to develop a new γ'

precipitation strengthening Ni base superalloy which has greater high-temperature strength and the foregoing various properties in a balanced manner.

However, it has not been of great ease to develop such a new alloy.

As the constituent elements comprising a γ' precipitation strengthening Ni base superalloy are known more than 10 elements, including Al, Co, Cr, Mo, W, Ti, Nb, Ta, and Hf, in addition to the Ni which is the base element. It costs much labor and time, and it was virtually infeasible, to produce alloys of different compositions by combining these 10 or more constituent elements, and verify all the properties of these. Even if the compositions of these constituent metal elements were varied in three steps, the resulting combinations would be as many as 3^9 , i.e., 19683. For the actual development of alloys, it is required to examine by varying compositions in more detail and the combinations will reach an exorbitant number.

Accordingly, it is desirable to conveniently and efficiently optimize the quantitative ratio of the phases constituting an alloy and the proportion of the constituent elements. However, only technology for determining harmful phases by the phase calculation in which the electron theory is applied, known as PHACOMP, is available, and no decisive measures have been found for the development of new alloys.

According to the present invention there is provided apparatus for determining the proportion of constituent elements of an alloy, for use in the production of a γ' precipitation

strengthening type Ni base superalloy which comprises a memory means having storing proportions of constituent elements of Ni base superalloy, an input means for entering the composition of an alloy and storing it into said memory means, a calculating means having structural factor equation and property equation for calculating structural factors from the alloy composition stored in said memory means and calculating properties from said alloy composition and the structural factors calculated, and a display means for displaying the structural factors and properties calculated by means of said calculating means together with the alloy composition.

Furthermore, there is also provided apparatus for determining the proportion of constituent elements of an alloy, for use in the production of a γ' precipitation strengthening type Ni base superalloy, which comprises a memory means storing proportions of constituent elements and structural factors of Ni base superalloy, an input means for entering one or more kinds of the required performance and storing them into said memory means, a calculating means having structural factor equation, and property equation, for calculating alloy composition from the required performance stored in said memory means, further calculating the structural factors and properties from the alloy composition calculated and storing them into said memory means together with the alloy composition, and a display means for displaying a list of the composition, structural factors and properties of an alloy calculated by said calculating means.

Some embodiments of the invention will now be described by way of examples and with reference to the accompanying drawings, in which:-

Fig. 1 is a block diagram illustrating the structure of a device for determining the composition of a precipitation strengthening Ni base superalloy according to the present invention.

Fig. 2 is a flow chart illustrating the system of the device as shown in Fig. 1.

Fig. 3 is a flow chart illustrating an embodiment of a part of the system of the analytical calculating system of the calculating means which determines the composition and quantitative ratio of γ phase and γ' phase.

Fig. 4 is a view illustrating a display indicating the equilibrium and various high-temperature properties at 900°C of the TMS-12 alloy obtained by the device according to the present invention.

Fig. 5 is a correlation drawing indicating the properties of the alloy designed by the device of the present invention together with the observed values and the properties of the conventional practical alloys and the existing developed alloys.

As shown in Fig. 1, a device for determining the composition of a γ' precipitation strengthening Ni base superalloy according to the present invention comprises a memory unit (1) for storing the constituent elements of the Ni base superalloy Ni, Co, Cr, Mo, W, Al, Ti, Nb, Ta, Hf, Re, Fe, C, B and Zr, an input unit (2) for entering the alloy

composition, or one of more kinds of required performance and storing them in the memory unit (1), a calculating unit (3)

Table 1

Structural factors	Properties
Composition of phases and ratio (at 900°C)	Normal cast alloy (polycrystalline) <ul style="list-style-type: none"> • Creep rupture resistance (at 1000°C, 12 kgf/mm²) • High-temperature tensile property (at 900°C) • High-temperature corrosion resistance
Phase stability	Single crystal alloy <ul style="list-style-type: none"> • Creep rupture resistance (at 1040°C, 14 kgf/mm²) • High-temperature corrosion resistance
Lattice constant of γ phase and γ' phase (at room temperature) and misfit (at room temperature and 1040°C)	Powder metallurgy or forge alloy <ul style="list-style-type: none"> • High-temperature tensile property (at 760°C) • High-temperature corrosion resistance
Specific gravity (at room temperature)	
Liquid phase line temperature and solid phase line temperature	
Initial melting point	
Temperature at which γ' phase becomes complete solid solution	

having the equation for calculating structural factors and the equation for calculating properties and having an analytical calculating system for calculating the structural factors from the alloy composition stored in the memory unit (1) and further calculating the alloy properties from said alloy composition and the structural factors calculated and a searching calculating system for calculating the alloy composition from the required performance stored in the memory unit (1), further calculating the structural factors and properties from the alloy composition calculated, and storing them in the memory unit (1) together with the alloy composition, and a display unit (4) for displaying a list of the structural factors and properties calculated by the analytical calculating system of the calculating unit (3) and the alloy composition entered, or a list of the alloy compositions, structural factors and alloy properties calculated by the searching calculating system of the calculating unit (3). Alloy composition data may if desired be directly supplied to apparatus for producing the alloy, to control the quantities of the constituent elements included in the alloy.

Table 1 shows the representative structural factors and properties which can be entered, and be calculated by this device.

As shown in Fig. 2, the device for supporting to design Ni base superalloy has two processes i.e., an analytical process (5) for automatically calculating the structural factors and properties of the alloy from the alloy composition entered, and outputting them, and a searching process (6) for automatically searching the alloy composition meeting the required performance entered and outputting it. Either the analytical process (5) or the searching process (6) is selected according to an object. This selection of either the analytical process (5) or the searching process (6) can be done with the input unit (2).

Now, description will be given as to the analysis of alloy properties and the searching of them according to the present invention, respectively.

Analysis of Alloy Properties

Alloy composition is entered with use of the input unit (2), the calculating unit (3) firstly calculates the compositions and quantitative ratios of carbides and borides.

When a Ni base superalloy is used as a polycrystalline material, C (carbon) and B (boron) are normally added as grain boundary strengthening elements. These C and B exist primarily in the grain boundary of the Ni base superalloy as carbides and borides, respectively. The carbides come in three types, MC, $M_{23}C_6$, and M_6C (M: metallic element) and borides in two types, M_3B_2 and M_5B_3 (M: metallic element).

The compositions and quantitative ratios of the carbides and borides which are formed in the alloy are calculated from the alloy composition entered, and they are deducted from the

alloy composition, and then the composition in the two phase regions of the γ phase (solid solution phase) and the γ' phase (Ni and Al metal compound phase) which are the principal constituent phases of the Ni base superalloy is obtain. If the Ni base superalloy is to be made a single crystalline material, its composition can be entered with the composition value of C and B as 0. The calculation equation for the composition and quantitative ratio of carbides and borides and for the composition of the two-phase region of γ phase and the γ' phase are stored in the memory unit (1).

Then, from the composition of the two-phase region of γ phase and γ' phase calculated, the composition and quantitative ratio of the γ phase and γ' phase, which have a great influence upon alloy properties, are determined based upon the equilibrium calculating equation stored in the calculating unit (3). As the calculating equilibrium equation, the super plane equation in which the composition of γ' phase is in equilibrium with γ phase exists, namely γ' face equation, and distribution ratio equation shown by the ratio of the concentration of i element in the γ phase to the concentration of i element in γ' phase are employed. Where i indicates Co, Cr, Mo, W, Al, Ti, Nb, Ta, Hf, Re and Fe.

The γ' face equation and the distribution ratio equation are prepared based upon the analytical data in which the existing developed Ni base superalloy is subjected to multiple regression analyses.

The γ' face equation is shown as a function of the

concentrations of the constituent elements in γ' phase as indicated in the following equation:

Al concentration in γ' phase

= f (the concentrations of Co, Cr, Mo, W, Ti, Nb, Ta, Hf, Re and Fe (at %) in γ' phase)

.... 1

The distribution ratio equation is shown as a function of the concentrations of the constituent elements in γ' phase as indicated in the following equation:

Distribution ratio of i element

= g_i (the concentrations of Co, Cr, Mo, W, Al, Ti, Nb, Ta, Hf, Re, and Fe (at %) in γ' phase)

.... 2

Where i indicates Co, Cr, Mo, W, Al, Ti, Nb, Ta, Hf, Re, and Fe.

Using these equations 1 and 2, an iterative convergence calculation based on the system flow as shown in Fig. 3 is performed to determine the composition and quantitative ratio of γ phase and γ' phase.

As shown in Fig. 3, the calculating unit (3) is provided with a loop (7) for making convergence calculation of the composition and distribution ratio of γ' phase from the quantity of γ' phase and the initial value of the distribution ratio, and another loop (8) for performing convergence calculation of the quantity of γ' phase, iterative convergence calculation by means of these loops (7) and (8) being performed in coordination.

This double iterative convergence calculation provides highly

accurate compositions and quantitative ratio of γ phase and γ' phase. In case where harmful phases are generated from the alloy composition entered or where the composition consists of γ phase alone and γ' phase is not precipitated, the display unit (4) as illustrated in Fig. 1 displays a message about that. In this case, the alloy composition is entered again to calculate composition and quantitative ratio of γ phase and γ' phase.

After the composition and quantitative ratio of γ phase and γ' phase are calculated, the other structural factors and properties as indicated in Table 1 are calculated. All the equations of structural factors and properties are stored in the calculating unit (3).

One of the features of the device according to the present invention is to make an equation of alloy properties a function of the compositions and structural factors of the alloy performed by multiple regression analyses of the existing data, thereby making it possible to calculate various alloy properties as indicated in Table 1 with the calculating unit (3).

The structural factors and alloy properties calculated are displayed on the display unit (4) together with the alloy composition entered, and may be used to control the alloy production process.

EXAMPLE 1

Entering the composition of TMS-12 alloy, the equilibrium at 900°C and various high-temperature properties were calculated. Fig. 4 is the results displayed on a display unit (4).

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The meanings of the abbreviated symbols indicated in Fig. 4 are
as in the following Table 2:

Table 2

Abbreviated symbols	Parameters or Properties		State
GP	γ' phase composition		900°C
G	γ' phase composition at%		900°C
ATPCT	Weight %		900°C
WT.PCT	γ' phase quantity (atomic quantity)		Room temperature
F.GP	Specific gravity		900°C
DENSITY	Solid solution index		Room temperature
SI	γ' lattice constant (A)		Room temperature
LAT.GP	γ' lattice constant (A)		Room temperature and 1040°C
LAT.G	Lattice misfit (%)		Room temperature and 1040°C
LM	γ' electron vacancy		900°C
NV.GP	γ' electron vacancy		900°C
NV.G	PHACOMP		900°C
NV.G-NVC	Liquid phase line temperature (°C)		900°C
LIQ	Solid phase line temperature (°C)		900°C
SOL1	Melting point temperature range (°C)		900°C
RANGE	Initial melting temperature (°C)		900°C
SOL2	Complete solid solution temperature (°C)		900°C
SOLV	Complete solid solution temperature range (°C)		900°C
WDW	High-temperature corrosion resistance due to crucible test (compared with IN 378 alloy)		900°C
H.COR.C	High-temperature corrosion resistance due to burner rig test (compared with IN 378 alloy)		850°C
H.COR.B	0.2% yield strength of normal cast alloy (kgf/mm ²)		900°C
YS	Tensile strength of normal cast alloy (kgf/mm ²)		900°C
UTS	Elongation at rupture of normal cast alloy (%)		900°C
EL	Creep rupture life of normal cast alloy (h)		1000°C, 12kgf/mm ²
LIFE.CC	Creep rupture life of single crystal alloy (h)		1040°C, 14kgf/mm ²
LIFE.SC	Specific strength of normal cast alloy (kgf/mm ²)/(gcm ³)		980, 100h
SPC.SRGHT			

* Lattice misfit (%) = [($a\gamma'$ - $a\gamma$)/ $a\gamma$] × 100 h

The calculated values of the structural factors and various properties of γ phase and γ' phase as depicted in Fig. 4 proved to be in good agreement with the observed values of TMS-12 alloy. The calculation time was approximately 2 seconds. It was confirmed that this device provided high-speed and highly accurate analyses of alloy properties.

Searching of Alloy Composition

As shown in Fig. 2, in searching for the composition of a new alloy with desired properties, a searching system (6) is selected by means of the input unit (2) and the required performance is entered. As the required performance, one or more of the alloy properties as listed in Table 1 can be chosen arbitrarily. Furthermore, one or more of the structural factors are selected and can be added to as the required performance.

When the required performance is entered through the input unit (2), γ' phase composition, γ' phase quantity, and the quantities of C, B and Z automatically vary bit by bit in the calculating unit (3) and the following calculations are automatically calculated for each of them.

Firstly, using the distribution ratio equation as described above, the distribution ratio is calculated from γ' phase composition and γ phase composition in equilibrium with γ' phase is calculated. Then, $(\gamma + \gamma')$ composition is calculated from γ' phase composition, γ' phase quantity and γ phase composition calculated, and the compositions and quantitative ratios of the carbides and borides in equilibrium with $(\gamma + \gamma')$ composition are calculated. Subsequently, the composition of $(\gamma$

+ γ') and those of carbides and borides are summed, the alloy composition being calculated.

In this way, the compositions of all alloys are searched.

As noted above, another feature of the device according to the present invention is to vary and set γ' phase composition and γ' phase quantity, and quantities of C, B and Zr, to calculate γ phase, carbides and borides successively, and to finally add them to calculate alloy composition. This permits accurate calculation of the alloy composition with varying them finely, and can also cut the calculation time remarkably because of no need to obtain the solution.

After the alloy composition has been calculated, the structural factors and properties for the composition are calculated as with the analytical process (5) as described above. Then, a comparison of these values obtained with the required performance entered is performed and if they meet the required performance, these values are ranked as necessary. The compositions, structural factors and properties of the alloy are stored in the memory unit (1), and a list of these alloy compositions, structural factors and properties are displayed on the display unit (4) for use in the production process. On the other hand, if the calculated values fail to meet the required performance, returning to the step of varying and setting γ' phase composition and γ' phase quantity as well as the quantities of C, B and Zr, the calculations for the alloy composition are repeated. If there is no alloy composition which meets the required performance, information about that is displayed on the display

unit (4). The foregoing process is also done automatically. The calculation time varies depending upon the steps in which γ' phase composition is varied, but it is generally about 30 minutes.

EXAMPLE 2

As the required performance, creep rupture life (test conditions: 1040 °C, 14 kgf/mm²) was set at 5000 hrs or longer, and specific gravity at 8.6 or lower, and certain limitations were placed on the range of temperature at which γ' phase becomes a solid solution and lattice constant misfit. Ni base alloy system consisting of the ten elements, Co, Cr, Mo, W, Al, Ti, Nb, Ta and Hf was searched for all combinations.

The search was completed in about 30 minutes, and a series of alloy compositions, structural factors and properties meeting the foregoing required performance obtained. Among them, the alloy having the longest creep rupture life is TMS-64 alloy (Cr:6.5%, Mo:8.4%, W:1.0%, Al:5.8%, and Ta:6.7%, with the remaining percentage occupied with Ni), and its creep rupture life was 7080 hours.

After this the alloy was actually melted, and a single crystal test specimen was prepared and was put to solution heat treatment in the designed range of temperatures at which γ' phase becomes a solid solution. Then, it was subjected to normal ageing treatment and the properties were measured. After that, the measured properties were compared with the designed values. The results are depicted in Fig. 5 together with the properties of practical alloys and the existing developed

alloys.

As is apparent from Fig. 5, it was confirmed that the designed value of creep rupture life of TMS-64 alloy is quite similar to the observed value, though the former shows a little longer life. TMS-64 was observed to show a longer creep rupture life than the practical alloy and the existing developed alloy, with the lower specific gravity. It was demonstrated that the device according to the present invention can well determine the composition of a new alloy.

EXAMPLE 3

The specific gravity was limited to 8.1 or lower and an alloy with the longest creep rupture life was searched. As a result, TSM-61 alloy (Ni base alloy containing Cr, Mo, Al, Ti, Nb and Ta) was designed, which had a creep rupture life of 1755 hours.

As in the example 2, this alloy was actually melted, a single crystal test specimen was prepared, and it was put to solution heat treatment in the designed range of temperatures in which γ' phase becomes a solid solution. Then, it was subjected to normal ageing treatment and the properties were measured. After that, the measured properties were compared with the designed values. This result was also shown in Fig. 5.

As in the case of TMS-64 alloy in example 2, it could be confirmed that the designed value of creep rupture life of TMS 61 alloy is quite similar to the observed value, though the former is somewhat longer. This alloy was observed to have a longer creep rupture life than the practical alloy and the

existing developed alloy, with the lower specific gravity.

It is needless to say that this invention is not limited to the above specific examples. Variations are made as to the types of structural factors and properties, the alloy compositions and required performance to be entered, the calculation time by the calculating unit and other details.

Claims

1. Apparatus for determining the proportion of constituent elements of an alloy, for use in the production of a ' precipitation strengthening type Ni base superalloy which comprises a memory means having storing proportions of constituent elements of Ni base superalloy, an input means for entering the composition of an alloy and storing it into said memory means, a calculating means having structural factor equation and property equation for calculating structural factors from the alloy composition stored in said memory means and calculating properties from said alloy composition and the structural factors calculated, and a display means for displaying the structural factors and properties calculated by means of said calculating means together with the alloy composition.
2. Apparatus as claimed in Claim 1, wherein the proportions of constituent elements stored in the memory means represent Ni, Co, Cr, Mo, W, Al, Ti, Nb, Ta, Hf, Re, Fe, C, B and Zr.
3. Apparatus as claimed in Claim 1 or 2, wherein the structural factor equation stored in the calculating means includes at least an equilibrium equation of γ phase and γ' phase.
4. Apparatus as claimed in Claim 3, wherein the equilibrium equation of γ phase and γ' phase consists of γ' face equation and distribution ratio equation.
5. Apparatus as claimed in any preceding Claim, wherein the property equation stored in the calculating means is indicated as function of the composition and structural factor of an alloy.

6. Apparatus as claimed in any preceding Claim, which has a calculating means for calculating the compositions and quantitative ratios of γ phase and γ' phase by coordinating the interative convergence calculation of the composition and the distribution ratio of γ' phase with that of γ' phase quantity.

7. Apparatus for determining the proportion of constituent elements of an alloy, for use in the production of a ' precipitation strengthening type Ni base superalloy, which comprises a memory means storing proportions of constituent elements and structural factors of Ni base superalloy, an input means for entering one or more kinds of the required performance and storing them into said memory means, a calculating means having structural factor equation, and property equation, for calculating alloy composition from the required performance stored in said memory means, further calculating the structural factors and properties from the alloy composition calculated and storing them into said memory means together with the alloy composition, and a display means for displaying a list of the composition, structural factors and properties of an alloy calculated by said calculating means.

8. Apparatus as claimed in Claim 7, wherein the proportions of constituent elements stored in the memory means represent Ni, Co, Cr, Mo, W, Al, Ti, Nb, Ta, Hf, Re, Fe, C, B and Zr.

9. Apparatus as claimed in Claim 7 or 8, wherein the structural factor equation stored in the calculating means includes at least an equilibrium equation of γ phase and γ' phase.

10. Apparatus as claimed in Claim 9, wherein the equilibrium equation of γ phase and γ' phase consists of γ' face equation and distribution ratio equation.

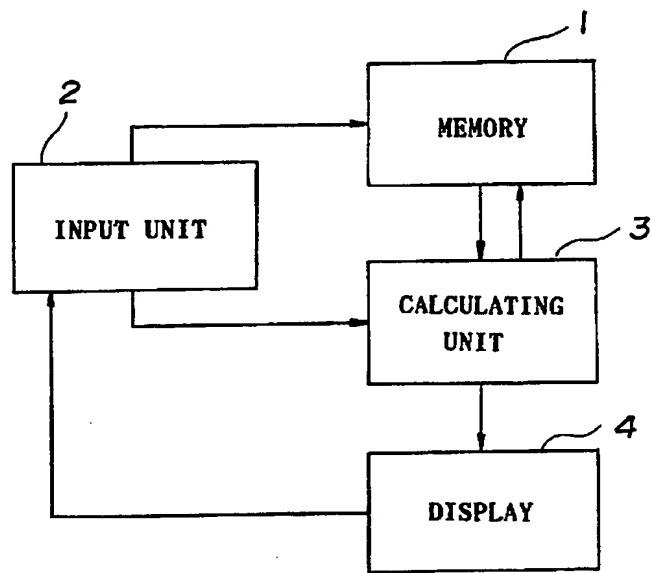
11. Apparatus as claimed in Claim 7, 8, 9 or 10 wherein the property equation stored in the calculating means is indicated as a function of the composition and structural factor of an alloy.
12. Apparatus as claimed in any of Claims 7 to 11, wherein the required performance are one or more of those selected from the properties and/or structural factors.
- 13.. Apparatus as claimed in any of Claims 7 to 11, which has a calculating means for calculating the alloy composition by way of steps in which the composition and quantity of γ' phase, and the quantities of C, B and Zr are caused to vary automatically, the compositions of γ phase, carbides and borides being calculated for each of them, and then these are summed up.
14. Apparatus as claimed in any of claims 7 to 13 including means for outputting composition data to directly control an alloy production process.
15. A method of making a γ' precipitation strengthening type Ni base superalloy using apparatus as claimed in any preceding claim, comprising inputting via said input means one or more kinds of required performance data and storing them into said memory means, carrying out an iterative search procedure using the structural factor equation and property equation and outputting values of the proportions of constituent elements of an alloy substantially satisfying the required performance.
16. Apparatus for determining the proportion of constituent elements of an alloy, for use the production of a γ' precipitation strengthening type Ni base super-

alloy, substantially as hereinbefore described with reference to the accompanying drawings.

17. A method of making a γ' precipitation strengthening type Ni base superalloy substantially as hereinbefore described with reference to the accompanying drawings.

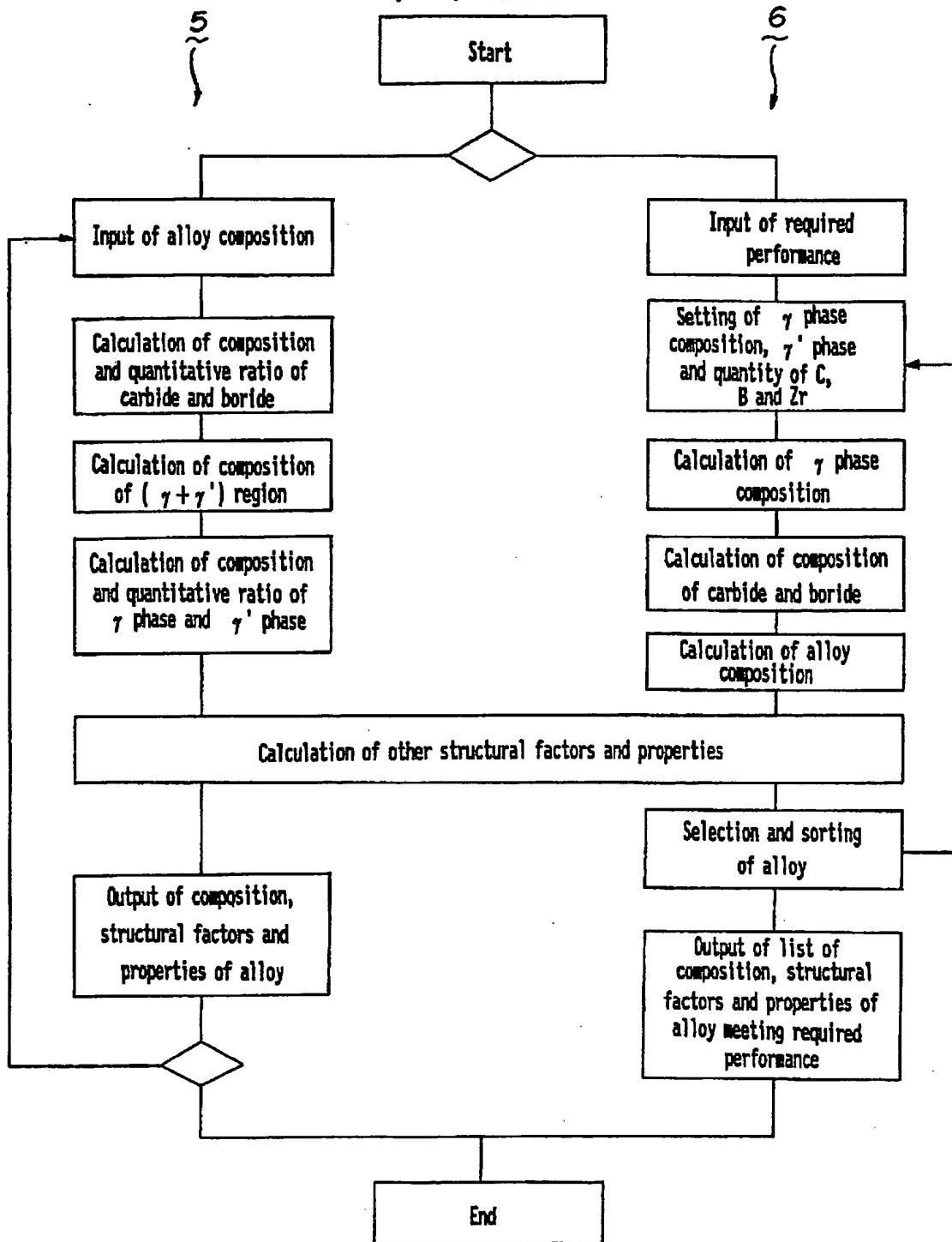
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FIG. 1



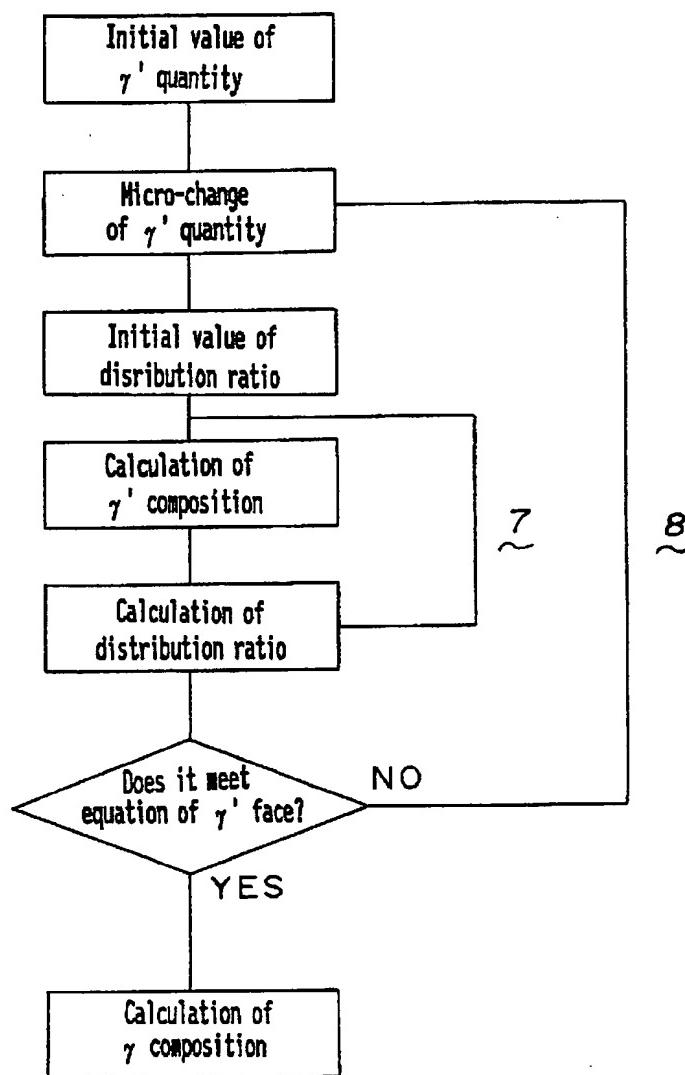
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FIG. 2



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FIG. 3



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TMS-12 ***** PHASE(AT 900.C) & PROPERTY CALCULATION *****											
ALLOY	NI	CO	CR	MO	W	AL	TI	NB	TA	HF	RE
GP	72.89	0.00	2.09	0.00	3.04	18.06	0.00	0.00	3.92	0.00	0.00
G	72.56	0.00	16.74	0.00	6.38	3.45	0.00	0.00	0.87	0.00	0.00
ATPCT	72.76	0.00	8.01	0.00	4.39	12.16	0.00	0.00	2.68	0.00	0.00
WTPCT	67.70	0.00	6.60	0.00	12.80	5.20	0.00	0.00	7.70	0.00	0.00
F.GP	LAT.GP(A)	NV.GP	LIQ(C)	SOL2(C)	H.COR.C	YS(KGF)	LIFE.CC(H)				
0.596	3.594	2.325	1411.4	1359.8	287.31		61.0				893.6
DENSITY	LAT.G(A)	NV.G	SOL1(C)	SOLV(C)	H.COR.B	UTS(KGF)	LIFE.SC(H)				
9.062	3.582	1.870	1396.3	1328.6	10.48		67.0				2327.3
SI	LM(%)	NV.G-NVC	RANGE(C)	WDW(C)	BBI	EL(%)	SPC.	STRGTH			
1.173	0.327	0.197	15.1	31.1	0.00	4.7		1.60			

***** TRY AGAIN? <YES(0) NO(1)>

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